Synthesis and catalytic properties of MIL-100(Fe), an iron(III) carboxylate with large pores†

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The large-pore iron(III) carboxylate MIL-100(Fe) with a zeotype architecture has been isolated under hydrothermal conditions, its structure solved from synchrotron X-ray powder diffraction data, while Friedel–Crafts benzylation catalytic tests indicate a high activity and selectivity for MIL-100(Fe).

The recent interest in the synthesis of hybrid inorganic–organic solids gives a new dimension to the domain of porous compounds.[1–4] They offer significant new scientific and technological opportunities[5] by combining attractive features of both inorganic and organic moieties and lead to many potential applications in gas storage,[6,7] catalysis,[8,9] insertion,[10,11] magnetism,[12,13] optical devices,[14] *etc.* Most of them are prepared using functionalized organic ligand (phosphonates, carboxylates, sulfonates...) and many elements in the Periodic Table have been incorporated in these new framework materials exhibiting novel structures not seen in zeolite chemistry. The introduction of 3d transition metals within the skeleton provides new electronic properties. Among them, iron is an environmentally benign and cheap component with non-toxicity and redox properties. However, to the best of our knowledge, while some MOF materials have been reported to date with iron(II) or iron(III),[15–20] only two of them combine a permanent porosity and large pores.[21,22] We report here the successful synthesis and structure determination of MIL-100(Fe) (MIL: Materials of Institut Lavoisier), a new scarce example of an iron(III) carboxylate with a large accessible and permanent porosity.

This solid was isolated as a polycrystalline powder from a reaction mixture of composition 1.0 Fe^0 : 0.66 1,3,5-BTC : 2.0 HF : 1.2 HNO_3 : 280 H_2O (1,3,5-BTC = benzene tricarboxylic or trimesic acid) that was held at 150 °C in a Teflon-lined autoclave for 6 days with a initial heating ramp of 12 h and a final cooling ramp of 24 h. The pH remains acidic (<1) throughout the synthesis. The light-orange solid product was recovered by filtration and washed with deionized water. A treatment in hot deionised water (80 °C) for 3 h was applied to decrease the amount of residual trimesic acid (typically, 1 g of MIL-100(Fe) in 350 ml of water) followed by drying at room temperature.

A laboratory powder X-ray diffraction pattern showed that crystalline phase had been produced, isostructural with the chromium carboxylate MIL-100(Cr).[23] Elemental analysis indicated that the contents of Fe, F, C and H (obs: 13.8% Fe, 1.3% F, 23.5% C) are in good agreement with the values based on the structure formula, $Fe^{III}{}_3O(H_2O)_2F\cdot\{C_6H_3(CO_2)_3\}_2\cdot nH_2O$ ($n \sim 14.5$) despite an excess of carbon content (calc.: 14% Fe, 1.8% F, 21.0% C). It has not been possible to prepare sizeable crystals for single-crystal diffraction studies whatever the synthesis conditions. Thermal analysis (TGA2050 TA apparatus, O_2 flow, heating rate 3 K min^{-1}) shows three weight losses between 298 and 873 K. The first ($\sim$40.1%) at 373 K is attributed to the departure of the free water molecules inside the pores. The second at 473 K ($\sim$4.5%) comes from the water molecules which interact with the iron trimers. The final weight loss ($\sim$35.3%) at 573 K is related to the combustion of the trimesic acid. These latter two losses are, on the whole, in agreement with the theoretical values (calc: 4.6 and 35.2%). Note that the free water content deduced from the structure determination ($\sim$29.5%) is slightly lower than the experimental value (TGA). This is due to the variable water content in MIL-100 solids which vary considerably depending on the atmospheric conditions.

The structure of title solid was solved from high-resolution synchrotron X-ray powder diffraction data using coordinates of MIL-100(Cr) as the starting model (ESI†).‡ The final Rietveld plot is shown in Fig. 1. MIL-100(Fe) is an iron(III) carboxylate built up from trimers of iron octahedra sharing a common vertex μ_3-O. The trimers are then linked by the benzene-1,3,5-tricarboxylate moieties in such a way that this leads to the formation of hybrid supertetrahedra which further assemble into a zeolitic architecture of the MTN type (Fig. 2). This delimits two types of mesoporous cages of free apertures of *ca.* 25 and 29 Å, accessible through microporous windows of *ca.* 5.5 and 8.6 Å. Bond valence calculations indicate a trivalent state of iron.

As is illustrated in Fig. 3, the transmission Mössbauer spectra recorded at 300 and 77 K consist of asymmetrical quadrupolar doublets with broadened and overlapped lines, in agreement with the large number of different environments of Fe atoms.[24] Whatever the fitting model, the isomer shift values (0.54 and 0.42 mm s^{-1} at 300 K and 77 K, respectively) remain consistent with the presence of high spin state of Fe^{3+} ions located in octahedral units. Taking into account the crystallographic structure, one might describe the spectra by means of seven

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† Electronic supplementary information (ESI) available: Crystallographic details, TGA, adsorption, Mössbauer and catalysis data. See DOI: 10.1039/b704325b

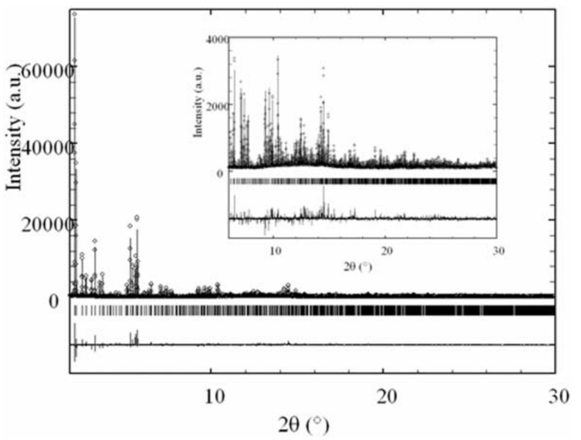

Fig. 1 Final Rietveld refinement plot for $Fe^{III}_3O(H_2O)_2F\cdot\{C_6H_3(CO_2)_3\}_2\cdot nH_2O$ (MIL-100(Fe)) in the space group $Fd\bar{3}m$. Observed, calculated and difference profiles are plotted on the same scale. Inset is an expanded region of a small part of the data.

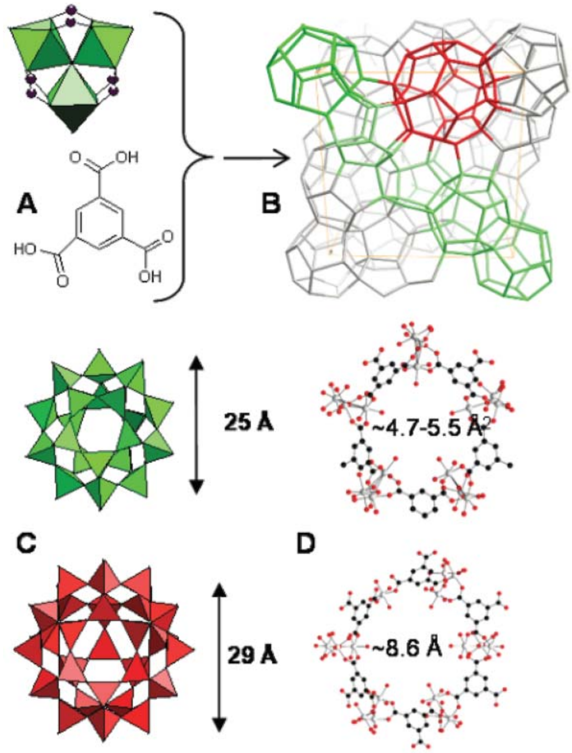

Fig. 2 Structure of MIL-100(Fe). (A) A trimer of iron octahedra and trimesic acid. (B) Schematic view of one unit cell of MIL-100(Fe). (C) the two types of cages in polyhedral mode. (D) Pentagonal and hexagonal windows in balls and sticks (Fe: grey; O: red; C: black).

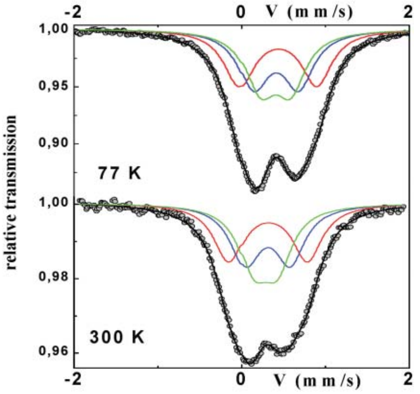

Fig. 3 Transmission Mössbauer spectra of MIL-100(Fe) recorded at 300 and 77 K.

different quadrupolar components: different solutions can be found without any clear and sound interpretation. On the contrary, assuming that three main types of Fe octahedral units can be distinguished according to their nearest chemical environments, this gives rise to a reasonable fitting model involving three quadrupolar components, as shown in Fig. 3. This could be explained by the presence of different fluorine environments for the iron atoms within the structure. It has been proved previously with the isostructural solid MIL-100(Cr) that the distribution of fluorine atoms bound to chromium atoms from the trimers, was at the origin of the three types of environments for the metal sites as evidenced by CO adsorption experiments.[25] Thus, as MIL-100(Fe) possesses the same fluorine composition as MIL-100(Cr), *i.e.* one fluorine atom per trimer, a similar environment is expected.

The different values of isomer shift confirm this hypothesis with some Fe ions mainly surrounded by O while the environment of others (with higher isomer shift) also contain F ions. The values of quadrupolar splitting (0.30, 0.52 and 0.90 mm s^{-1}) are consistent with different degrees of distortions and the highest distorted octahedral unit contains F anions. Finally, the significant increase of the absorption spectral area when decreasing the temperature should be noted. This is due to a large increase of the Debye–Waller factor, resulting from the strengthening of the structure, particularly due to its hybrid character which is temperature sensitive.

The permanent porosity of the new solid was measured by N_2 adsorption experiments performed in liquid nitrogen. MIL-100(Fe) revealed an adsorption isotherm characteristic of microporous solids (Fig. 4). However, due to the presence of two types of microporous windows and mesoporous cages with different sizes, two secondary uptakes at *ca.* $P/P_0 = 0.06$ and 0.12 can be distinguished from the isotherm, in agreement with our previous results with MIL-100(Cr).[23] The corresponding Langmuir surface area is estimated to be >2800(100) $m^2\ g^{-1}$. This value is, on the whole, in agreement with that of the isostructural solid MIL-100(Cr) ($S = 3100\ m^2\ g^{-1}$). The thermal stability of MIL-100(Fe)

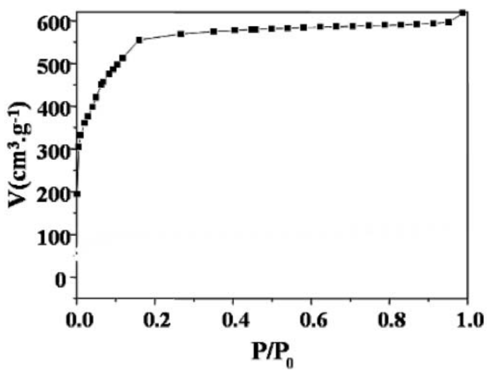

Fig. 4 N_2 adsorption isotherm of MIL-100(Fe) at 77 K (P_0 = 1 atm).

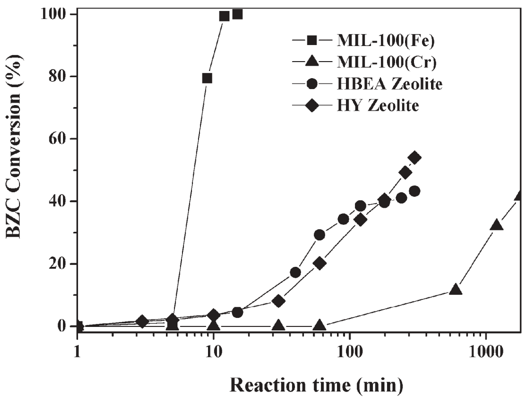

Fig. 5 Benzyl chloride conversion in the Friedel–Crafts benzylation of benzene over different catalysts. *Reaction conditions*: 70 °C, 7.8 ml benzene, benzene/benzyl chloride = 10 (molar ratio), 0.1 g catalyst.

has been studied by X-ray thermodiffractometry and reveals that this solid is stable up to 270 °C.

The use of heterogeneous catalysts in the liquid phase is highly desirable for Friedel–Crafts type reactions[27] because the use of conventional homogeneous catalysts for these reactions leads to several problems, such as difficulty in separation and recovery, disposal of spent catalyst and corrosion. In the light of the importance of heterogenous catalysis, we have performed Friedel–Crafts benzylation to confirm the suitability of iron-containing MIL-100 as a new porous catalyst (see ESI†). Fig. 5 shows the conversion of benzyl chloride in the liquid phase benzylation of benzene by benzyl chloride (BZC) to diphenylmethane (DPM) at 70 °C over MIL-100(Fe), MIL-100(Cr) and zeolite catalysts for comparison. We find that MIL-100(Fe) gives high activity and selectivity, showing 100% BZC conversion [*X*(BZC)] with nearly 100% DPM selectivity [*S*(DPM)] being quickly attained after a short induction period (5 min). By contrast, MIL-100(Cr) was poorly active for the reaction, *i.e.*, 42% *X*(BZC) after 30 h. Solid acid catalysts such as HBEA and HY zeolites were not so active under the same reaction conditions: 43.4% *X*(BZC) with 97.6% *S*(DPM) for HBEA and 54.0% *X*(BZC) with 95.8% *S*(DPM) for HY after 5 h. These results clearly indicate that iron species in MIL-100(Fe) play a role as catalytically active sites in Friedel–Crafts alkylation. The observed high benzylation activity of MIL-100(Fe) might be attributed to the redox property of trivalent iron species ($Fe^{3+} + e^- \leftrightarrow Fe^{2+}$) to play a significant role in activating both the reactants, consistent with results observed in iron-containing solid catalysts.[26–28] The origin of the induction period in the benzylation is generally ascribed to the inhibition effect by moisture present in the catalyst and/or in the reaction mixture[26] or the diffusion limitation of reactant molecules into the active site in the pore.

In summary, we report the synthesis and characterisation of a new example of a large-pore iron(III) carboxylate under hydrothermal conditions. First catalytic experiments suggest that iron(III) species metal sites are particularly interesting in catalysis and might lead to new applications. We are currently surveying phases produced from other iron(III) carboxylate systems.

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Notes and references

‡ Coordinates of MIL-100(Fe) have been deposited with the CCDC data bank, deposition number CCDC 640536. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704325b

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